Research Networking Programmes

Science Meeting – Scientific Report

The scientific report (WORD or PDF file - maximum of seven A4 pages) should be submitted online within two months of the event. It will be published on the ESF website.

Proposal Title: Materials Challenges in Devices for Fuel Solar Production and Employment

Application Reference N°: 5236

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Organizers:

Thomas Bligaard (Stanford University, U.S.A.)

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1) Summary (up to one page)

The production and distribution of energy from renewable energy sources are key components of sustainable development. In this context, efficient energy storage, e.g. by converting solar into chemical energy in the form of hydrocarbons, and conversion efficiency become key issues. To this aim, understanding and controlling processes in functional materials relevant for photoelectrochemical and fuel cells is essential to increase the efficiency of these devices. Our workshop brought together experimentalists and theoreticians to analyze the state of the art in the field, to highlight to most relevant open problems and to identify those that could be attacked in the near future with the existing techniques. Attention has been devoted to address physico-chemical problems at the electrode/electrolyte interface, and materials challenges at

the electrode. These involve phenomena such as photoabsorption, (photo-)catalytic reactions, excess charge transport, vacancy transport, proton transport.

The importance of connecting theory and experiment has been stressed, while noticing that a fruitful exchange between theory and experiment, but also between experiments on model systems and experiments on industrial systems is always a long-term endeavour that might need years to bring fruits, but which is necessary to bring the field forward. Microscopic phenomena are still poorly understood. For example, recombination centers in oxides and the origin of photocatalytic activity are still not understood. In this field, the contribution of theory is still insufficient. We need concepts about microscopic phenomena that give insight and can guide materials search and research. At nanoscopic level, control of (nano-)structure formation is a desirable goal and a promising route to improve performance and durability. At the nanoscale many phenomena are new and/or uncontrolled. This size is not easy to reach for electronic structure calculations, so the models are often far from experiment. Finally, microstructure control is also essential to induce optimal porosity and thermal stability. For theory, there is a range of problems that need a more accurate and realistic description of the relevant materials and processes: open-shell radicals, charged states, and excited states. And then there is the need to deal with complex phase spaces, modelling high-barrier reaction by rare-event techniques, modelling chemically aggressive, often hot, reactive environment by ab-initio molecular dynamics, modelling component chemo-mechanics, going beyond explicit electrons, beyond dynamics (Monte Carlo techniques), beyond atomistic representations (embedding technique with "message-passing" multi-scale modelling).

2) Description of the scientific content of and discussions at the event (up to four pages)

The event covered the main approaches to functional materials for photoelectrochemical and fuel cells, including inorganic, (bio-)organic and hybrid materials. The latter represent a novelty of the last years, particularly the perovskite materials. For these materials, issues concerning their functional behaviour and their durability have been addressed. Photoabsorption, charge transport, ion transport, photo- and electro-catalysis are the main processes contributing their activity. Regarding the durability of the materials and of the devices, thermal processes, chemo-mechanical, chemical processes like poisoning, phase segregation contribute to the degradation of the materials.

<u>Functional properties of materials:</u>

Several materials choices have been considered, inorganic, (bio-)organic and hybrid materials. The hybrid materials are relative newcomers to the field and are rapidly showing improvements, specially the perovskite hybrid materials.

Among inorganic materials, Kevin Sivula discussed the potentiality and limits of hematite as a material for solar water splitting and hydrogen production. The material is abundant and stable, but it has a long photon penetration depth together with a short hole diffusion distance, as well as a high overpotential for water oxidation. He suggested overcoming some of these defects by aggressive substitutional doping and nanostructuring. Oomman Varghese has shown that a system of copper nanoparticles on titania nanotubes is able to transform carbon dioxide and water into hydrocarbons with interesting conversion rates. Paolo Fornasiero discussed the design of efficient inorganic catalysts, using core-shell structures. In particular, this design makes it possible to enhance the long-term stability of palladium catalysts for fuel cells, by building a protective ceria shell. Emiliana Fabbri discussed recent progress in the characterization of supported platinum catalysts for polymer fuel cells. Philipp Furler presented a ceria-based catalyst that exploits solar energy to achieve a highly efficient thermochemical conversion of carbon dioxide and water to hydrocarbons.

Serdar Sariciftci presented recent progress in the employment of organic and bioorganic systems for solar energy harvesting and conversion, where the control of the nanomorphology makes it possible to maximize the interaction between donor and acceptor molecules in an organic system. He also pinpointed interesting, simple molecules with good photoadsorption properties, such as caffeine, beta-carotene, the natural co-polymer shellac, the indigo dye and the Tyrian purple dye. Davide Bonifazi explored the possibilities to organize photoactive materials through self-assembly. Maurizio Prato reviewed recent progress in carbon-based materials for water splitting and electrocatalysis. Michele Aresta presented advanced hybrid systems, including enzymes, for the reduction of carbon dioxide to methanol and other high-value compounds.

Progress has also taken place in the investigation of the dynamics of excited charges by ultrafast spectroscopy. Giulio Cerullo presented results on ultrafast spectroscopy of light-harvesting systems. He investigated charge transfer in the photosynthetic unit of purple photosynthetic bacteria, as well as in artificial supramolecular systems, e.g. dyads composed by a carotenoid and a porphyrine, characterizing in detail the transitions involved.

<u>Long-term stability of materials and devices:</u>

To understand these issues, the challenge is to characterize the active material and to understand processes in-operando, including degradation processes responsible for activity loss. This requires advancement in techniques, both theoretical and experimental, as well as

significant interaction between them. In this context, of great significance are the recent developments of x-ray microscopic techniques, which make it possible to investigate the material in-operando at high spatial and temporal resolution, characterizing the chemical evolution of the materials during the catalytic process itself. Maya Kiskinova has shown how this technique helped characterizing degradation and corrosion processes in a fuel cell model involving a nickel electrode. Enrico Traversa presented novel materials with increased long-term stability for the proton transport in solid-oxide fuel cells. Theory is also making progress in the investigation of chemo-mechanical processes responsible for materials fracture, such as stress-corrosion cracking. This progress, presented by James Kermode, relies on advancement in computational methods, due to the intrinsic multi-scale nature of the problem. Therefore this kind of phenomena can only be studied with hybrid simulation methods that use quantum mechanics only when and where it is strictly necessary, i.e. for bond making and breaking. The method presented is the Learn-On-The-Fly (LOTF) method, which combines classical molecular dynamics with first-principles calculations in an efficient way. Studies of brittle fracture have been shown.

Computational methods:

The main efforts are devoted to address the complexity of real systems, with extended configuration spaces and interactions with the environment. Karsten Albe and Richard Catlow showed how first-principles simulations are able to describe point defect formation in semiconductor, and to predict band alignment at interfaces. Cristiana Di Valentin investigated redox process in titania and at its surfaces, by means of first-principles methods. It is important to describe exchange and correlation accurately enough, by employing DFT+U or hybrid functionals, to be able to describe localized charges such as polarons.

Karsten Jacobsen presented approaches based on high-throughput screening of materials for water splitting. This involved calculating thermodynamic stability and band gaps of several oxide compounds with the perovskite structure, as taken from the Inorganic Crystal Structure Database. Calculations of stability must be performed with respect to the metals and to other oxides with the same elements. Moreover, stability in water was also considered as a function of pH and bias. Regarding the gap, interesting materials for water splitting should have a gap in the range of 1.5-3 eV.

Timo Jacob and Simone Piccinin presented studies of surfaces and catalysts in an electrochemical environment. Big efforts are under way to include the effects of a realistic electrochemical environment. Nicola Marzari presented a new self-consistent continuum solvation model, and employed to investigate the equilibrium shape of nanoparticles in an electrochemical environment.

James Kermode presented the Learn-On-The-Fly approach to multi-scale atomistic modeling of materials, with a core region where quantum calculations are performed and a much larger simulation cell where atom dynamics is described by a force field. This technique has been applied to study fracture problems. Maurizio Fermeglia showed how to implement multi-scale simulation methods able to bridge the gap between the atomistic scale and the mesoscopic scale, and how to employ them to perform bottom-up design of polymeric structures.
Paolo Umari and Jochen Blumberger showed recent developments in the treatment of the electronic properties of materials, for excited states and charge transport respectively, and presented results for materials of interest for solar energy applications.

Discussion:

There is a need to better understand the fundamental processes (catalysis steps, overpotentials causes, hole/electron diffusion,...), to identify new, better-performing materials (we are still far from the thermodynamic limits). To this aim, there is need for better characterization through new and/or better techniques (experimental and computational), and a need to enhance component durability (against corrosion, performance deterioration, thermal fatigue,...). In particular, there is a need to have better in-situ and in-operando characterization techniques.
At atomistic level, doping is still the most promising route to enhance materials properties for photo- and electro-catalysis, to moderate overpotentials and enhance conductivity. Still, microscopic phenomena are still poorly understood. For example, recombination centers in oxides and the origin of photocatalytic activity are still not understood. In this field theory still has significant challenges to address, both in terms of accuracy and in terms of conceptual framework. We need to extend existing concepts related to microscopic phenomena and devise computational methods that are fast and accurate enough to give detailed insights and guide materials search and design.
At nanoscopic level, control of (nano-)structure formation is a desirable goal and a promising route to improve performance and durability. At the nanoscale many phenomena are new and/or uncontrolled. This size is not easy to reach for electronic structure calculations, so that often the models are far from experiment.
Finally, microstructure control is also essential to induce optimal porosity and thermal stability.

3) Assessment of the results and impact of the event on the future directions of the field (up to two pages)

Trends that are observed in the field, and are particularly promising are a shift towards (bio-)organic materials for enhanced range of functionalities, a shift towards mixing top-down and bottom-up fabrication strategies, trying to exploit supramolecular self-assembly. Synthesizing carbon-based fuels is a realistic option. Tight interaction of experiment and theory is essential, as e.g. catalysis is too hard to understand and control by either alone. Robert Schlögl proposes the activities at the Fritz-Haber-Institute in Berlin as best practice: collaboration between theory and experiment to understand the behavior of a model catalyst at the atomistic level, before moving the gained knowledge to investigate the more complex industrial catalyst. For such a collaboration to be successful, two elements are crucial: accuracy of results, and flow of ideas in both directions. Theory could help experimentalists focusing on most promising systems/measurements, but clear predictions from theory are needed. For theory, there is a range of problems that need a more accurate and realistic description of the relevant materials and processes: open-shell radicals (need of exact exchange techniques, to be benchmarked against higher-accuracy methods in small systems), charged states (non-periodic static embedding, image-charge corrections), excited states (advanced electronic-structure methods, models for transport in hole/electron conduction, e.g. in oxides). And then there is the need to deal with complex phase spaces (data mining, databases), modelling high-barrier reaction by rare-event techniques (NEB, metadynamics), modelling chemically aggressive, often hot, reactive environment by ab-initio molecular dynamics, modelling component chemo-mechanics (dynamical embedding), going beyond explicit electrons (force field potentials, cluster expansion), beyond dynamics (Monte Carlo techniques), beyond atomistic representations (embedding technique with "message-passing" multi-scale modelling).

The event has been a discussion forum among key players in the field, and has raised awareness among the participants about the challenges in the field, contributing also to bridge the gap among scientists working in different, but related fields, specially between theoreticians and experimentalists.

4) Annexes 4a) and 4b): Programme of the meeting and full list of speakers and participants

Annex 4a: Programme of the meeting

Monday, 19 May 2014

8.30-9.45 Registration and Administrative Formalities
9.45-10.00 Welcome
Session: Fuel cells

10.00–11.00 Maya Kiskinova
11.00 - 11.30 Coffee break
11.30 - 12.30 Emiliana Fabbri
Lunch Break
13.45 - 14.45 Peter Strasser
Session: Computational materials science
14.45 - 15.45 Richard Catlow
15.45 – 16.00 Coffee break
16.00 – 17.00 James Kermode

Tuesday, 20 May 2014
Session: Solar fuels I
9.00 – 10.00 Oomman Varghese
10.00 - 10.30 Coffee break
10.30 - 11.30 Kevin Sivula
11.30 - 12.30 Paolo Fornasiero
Lunch Break
Session: Simulations of photoelectrochemical reactions
13.45 -14.45 Karsten Jacobsen
14.45 - 15.45 Simone Piccinin
15.45 - 16.00 Coffee break
16.00 – 17.00 Timo Jacob
19.00 – 22.00 Poster session

Wednesday, 21 May 2014
Session: Solar fuels II
9.00 – 10.00 Michele Aresta
10.00 - 10.30 Coffee break
10.30 - 11.30 Erik Vesselli
11.30 - 12.30 Philipp Furler
Lunch Break
Session: Simulations of materials and reactions from the atomistic to the macro-scale
13.45 - 14.45 Cristiana Di Valentin
14.45 - 15.45 Karsten Albe
15.45 - 16.00 Coffee break
16.00 – 17.00 Maurizio Fermeglia

Thursday, 22 May 2014
Session: Organic materials
9.00 - 10.00 Davide Bonifazi
10.00 - 10.30 Coffee break
10.30 - 11.30 Serdar Sariciftci
Session: Photoabsorption
11.30 - 12.30 Paolo Umari
Lunch Break
Session: Solar fuels III
13.45 - 14.45 Robert Schlögl
14.45 - 15.00 Coffee break

15.00 – 17.00 Round table

Friday 23, May 2014
Session: Electrochemistry
9.00 – 10.00 Nicola Marzari
10.00 - 10.30 Coffee break
Session: Ion and charge transport
10.30 - 11.30 Enrico Traversa
11.30 - 12.30 Jochen Blumberger
Lunch Break
14.00 – 15.00 Giulio Cerullo
15.00 - 15.15 Coffee break
Session: Organic Materials
15.15 - 16.15 Maurizio Prato
16.15 - 16.45 Final considerations

Annex 4b: Full list of speakers and participants

Speakers:

Karsten Albe (TU Darmstadt, Germany)
Michele Aresta (University of Bari, Italy)
Jochen Blumberger (University College London, United Kingdom)
Davide Bonifazi (University of Namur, Belgium and University of Trieste, Italy)
Richard Catlow (University College London, United Kingdom)
Giulio Cerullo (Politecnico di Milano, Italy)
Cristiana Di Valentin (University of Milano-Bicocca, Italy)
Erik Vesselli (CNR-IOM, Italy)
Emiliana Fabbri (Paul Scherrer Institute, Switzerland)
Maurizio Fermeglia (University of Trieste, Italy)
Paolo Fornasiero (University of Trieste, Italy)
Philipp Furler (ETH Zurich, Switzerland)
Timo Jacob (University of Ulm, Germany)
Karsten Jacobsen (Technical University of Denmark, Denmark)
James Kermode (King's College London, United Kingdom)
Maya Kiskinova (Sinctrotrone Trieste, Italy)
Nicola Marzari (EPFL, Switzerland)
Simone Piccinin (CNR-IOM, Italy)
Maurizio Prato (University of Trieste, Italy)
Serdar Sariciftci (Johannes Kepler University Linz, Austria)

Robert Schlögl (FHI-MPG, Germany)
Kevin Sivula (EPFL, Switzerland)
Peter Strasser (TU Berlin, Germany)
Enrico Traversa (KAUST, Saudi Arabia)
Paolo Umari (University of Padova, Italy)
Oomman Varghese (University of Houston, U.S.A.)

Other participants:

Mohamad Khaled Aljoumaa (Atomic Energy Commission, Syria)
Naveed Ul Hassan Alvi (TU Madrid, Spain)
Ali Akbar Ashkarran (University of Mazandaran, Iran)
Manmadharao Banki (IIT Madras, India)
Alessandro Beltram (University of Trieste, Italy)
Federico Bianchini (King's College London, United Kingdom)
Susanna Bosi (University of Trieste, Italy)
Marco Caccin (King's College London, Italy)
Beatriz Helena Cogollo Olivo (University of Cartagena, Colombia)
Abdul Ardo Buba Dahiru (University of Abuja, Nigeria)
Christian Ecke (LMU Munich, Germany)
Matteo Farnesi Camellone (CNR-IOM, Italy)
Estefania German (Universidad Nacional del Sur, Argentina)
Angela Giuliani (University of Trieste, Italy)
Otto Emiliano Gonzalez Vazquez (ICTP, Italy)
Luca Grisanti (ICTP, Italy)
Pierre Guiglion (University College London, United Kingdom)
Ildiko Harsanyi (Hungarian Academy of Sciences, Hungary)
Fawzy Abdelhamid Mahmoud Hassan (National Research Center, Egypt)
Daniel Iglesias (University of Trieste, Italy)
Neama Gomaa Imam (Atomic Energy Authority, Egypt)
Dier Adil Jameel (University of Nottingham, United Kingdom)
Hossein Kalhori (Isfahan University of Technology, Iran)
Muhammad Kamran (Leiden University, The Netherlands)
Jinesh Kochupurackal (Indian Institute of Space-Science and Technology, India)
Lokesh Koodlur Sannegowda (Krishnadevaraya University, India)
Sunil Singh Kushvaha (CSIR-National Physical Laboratory, India)